APPLICATION UNDER UNITED STATES PATENT LAWS

Attorney Docket No.   021123-0238397

Invention: PRECIPITATED SILICAS

Inventor(s):   ESCH *ET AL.*

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This is a:

☐ Provisional Application

☐ Regular Utility Application

☐ Continuing Application

☐ PCT National Phase Application

☐ Design Application

☐ Reissue Application

☐ Plant Application

☒ Substitute Specification

☐ Marked up Specification

SPECIFICATION

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PRECIPITATED SILICAS

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation of U.S. Patent Application Serial No. 08/594,327, filed January 30, 1996 (now abandoned), which is a continuation of U.S. Patent Application Serial No. 08/319,490, filed October 7, 1994 (now abandoned), which in turn claims priority to German Patent Application No. P 44 27 137.9, filed July 30, 1994 and German Patent Application No. P 43 34 201.9, filed October 7, 1993. All applications are incorporated herewith in their entirety by reference.

BACKGROUND OF THE INVENTION

1.   Field of the Invention:

[0001]   The present invention relates to precipitated silicas, to the process for the production thereof and to the use thereof in rubber compounds.

2.   Background of the Invention:

[0002]   Precipitated silicas may be incorporated into rubber compounds (Wolff, *Kautschuk und Gummikunstst.* 41(7), 674 – 698, 1988). Known silicas may be only very poorly dispersed in rubber compounds, particularly at high filling rates. This poor dispersibility is one of the reasons why elevated silica filling rates are used only rarely in tire compounds. One reason for poor dispersibility may lie in the process by which the precipitated silicas are produced. Drying, poor grinding or also excessively hard granulation may lead to silica particles which cannot readily be dispersed (filler flecks). These flecks may be seen with the naked eye.

[0003]   Furthermore, silicas are highly polar and therefore have only poor phase compatibility with the non-polar polymers in the rubber compound. This form of dispersion occurs on the basis of the silica aggregates. It may only be evaluated using a light microscope and is known as microdispersion.

[0004]   Precipitated silicas which may be used as a filler in rubber compounds for tires are known from EP-A 0 520 862.

[0005]   A precipitated silica is known from published European Patent Application EP-A 0 157 703 which, according to EP-A 0 501 227, may be used as a filler in rubber compounds for tires.

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[0006]   Known precipitated silicas have the disadvantage that they exhibit poor microdispersion.

SUMMARY OF THE INVENTION

[0007]   The object of the invention is to provide a precipitated silica with optimum phase compatibility with rubber, polymer, and good microdispersion.

[0008]   The present invention provides a precipitated silica characterized by the following physicochemical properties:

BET surface area	35 m^2/g to 350 m^2/g
BET/CTAB surface area ratio	0.8 to 1.1
Pore volume, PV	1.6 ml/g to 3.4 ml/g
Silanol group density (V_2 = NaOH consumption)	3 ml/(1.5 g) to 9.5 ml/(1.5 g)
Average aggregate size	250 nm to 1500 nm
CTAB surface area	30 m^2/g to 350 m^2/g
DBP value	150 ml/100 g to 300 ml/100 g
V_2/V_1 by Hg porosimetry	0.19 to 0.46
preferably	0.20 to 0.23
DBP/CTAB	1.2 to 3.5

[0009]   The physicochemical properties are determined using the following measurement methods:

BET surface area	Areameter, Ströhlein, to ISO 5794/ Annex D
Pore volume	Mercury porosimetry to DIN 66 133 (7 bar to 2000 bar)
Silanol group density	in Sears values, according to Sears, *Anal. Chem.* **28(12)**, 1981 – 1983, 1956.
Average aggregate size	Photon correlation spectroscopy, determined by Zeta Sizer 3 (manufacturer: Malvern Instruments)
CTAB surface area	at pH 9, according to Janzen *et al.*, *Rubber Chem. Technol.* **44**, 1287 – 1296, 1971.
DBP value	ASTM D 2414-88

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Hg porosimetry   DIN 66 133

[0010]   The precipitated silica according to the invention may in particular have the following physicochemical parameters:

BET surface area $[m^2/g]$	Hg porosimetry [ml/g]	Sears value V_2 NaOH [ml/(1.5 g)]	Average aggregate size [nm]
35 to 100	2.5 to 3.4	3 to 5.8	900 to 1500
100 to 150	2.4 to 3.2	4 to 7.2	400 to 850
150 to 200	1.6 to 2.4	5.3 to 9.1	300 to 550
200 to 350	1.6 to 2.3	5.8 to 9.5	250 to 520

[0011]   In a preferred embodiment, the precipitated silica according to the invention has good grindability. This characteristic is represented by the average particle size determined using Malvern laser diffraction (D(4.3)) of ≤ 11 μm, in particular of ≤ 10 μm, measured after grinding on an Alpine Kolloplex pin impact mill (Z 160) at a throughput of 6 kg/h.

[0012]   The present invention also provides a process for the production of the precipitated silica with the following physicochemical parameters

BET surface area	$35 \ m^2/g$ to $350 \ m^2/g$
BET/CTAB surface area ratio	0.8 to 1.1
Pore volume, PV	1.6 ml/g to 3.4 ml/g
Silanol group density (V_2 = NaOH consumption)	3 ml/(1.5 g) to 9.5 ml/(1.5 g)
Average aggregate size	250 nm to 1500 nm
CTAB surface area	$30 \ m^2/g$ to $350 \ m^2/g$
DBP value	150 ml/100 g to 300 ml/100 g
V_2/V_1 by Hg porosimetry	0.19 to 0.46
preferably	0.20 to 0.23
DBP/CTAB	1.2 to 3.5

[0013]   which is characterized in that alkali silicate is reacted with mineral acids at temperatures of 60°C to 95°C while maintaining a pH of 7.5 to 10.5 and continuously

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stirring, the reaction is continued to a solids concentration in the precipitation suspension of 90 g/1 to 120 g/1, the pH value is adjusted to a value of less than or equal to 5, the precipitated silica filtered out, washed, dried and optionally ground or granulated.

[0014]   In a preferred embodiment, customary commercial sodium water glass may be diluted with water to a pH of 8 to 9 and concentrated sulfuric acid and the same water glass solution may simultaneously be added to this diluted water glass solution which has an SiO_2 content of 4.9 g/1, while maintaining the pH value of 8 to 9.

[0015]   Other preferred ranges of the pore volume ratio (V_2/V_1) are 0.19 to 0.43, 0.19 to 0.32, and 0.19 to 0.28.

[0016]   Simultaneous addition of water glass solution and sulfuric acid may be performed over a period (duration of precipitation) of up to 160 minutes, preferably of greater than 90 minutes, in particular within 30 minutes to 90 minutes.

[0017]   Depending upon the duration of precipitation, differing BET surface areas of the precipitated silica may be achieved. Thus, at a duration of precipitation of more than 90 minutes, surface areas of 35 m^2/g to 150 m^2/g are achieved and, at a duration of 30 minutes to 90 minutes, surface areas of 150 m^2/g to 350 m^2/g.

[0018]   The precipitated silica according to the invention may be modified with organosilanes of the formulas I to III

$$[R^1_n-(RO)_{3-n}Si-(Alk)_m-(Ar)_p]_q[B] \quad \text{(I)}$$
$$R^1_n-(RO)_{3-n}Si-(Alkyl) \quad \text{(II)}$$
$$\text{or}$$
$$R^1_n-(RO)_{3-n}Si-(Alkenyl) \quad \text{(III)}$$

in which:

B:	means $-SCN$, $-SH$, $-Cl$, $-NH_2$ (if q = 1) or $-S_x-$ (if q = 2)
R and R^1:	mean an alkyl group with 1 to 4 carbon atoms, the phenyl residue, wherein all residues R and R^1 may each have the same or different meaning
R:	means a C_1-C_4 alkyl, C_1-C_4 alkoxy group
n:	means 0, 1 or 2
Alk:	means a divalent unbranched or branched hydrocarbon residue with 1 to 6 carbon atoms
m:	means 0 or 1

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Ar:	means an arylene residue with 6 to 12 carbon atoms, preferably 6 carbon atoms
p:	means 0 or 1, providing that p and n do not simultaneously mean 0
x:	means a number from 2 to 8
Alkyl:	means a monovalent unbranched or branched unsaturated hydrocarbon residue with 1 to 20 carbon atoms, preferably 2 to 8 carbon atoms
Alkenyl:	means a monovalent unbranched or branched unsaturated hydrocarbon residue with 2 to 20 carbon atoms, preferably 2 to 8 carbon atoms

[0019]   Modification with organosilanes may be performed in mixtures of 0.5 parts to 50 parts of organosilanes, related to 100 parts of precipitated silica, in particular of 2 parts to 15 parts, related to 100 parts of precipitated silica, wherein the reaction between the precipitated silica and silane may be performed during compounding (*in situ*) or outside the compounding process (premodified).

[0020]   In a preferred embodiment of the invention, bis(triethoxy-silylpropyl) tetrasulphane may be used as the silane.

[0021]   The precipitated silica according to the invention may be incorporated into vulcanizable rubber compounds as a reinforcing filler in quantities of 5 parts to 200 parts, related to 100 parts of rubber, as a powder, microbeads or granules both with and without silane modification.

[0022]   One or more of the above-stated silanes may be added, together with the silica according to the invention, to the rubber compound, wherein the reaction between the filler and silane proceeds during the compounding process at elevated temperatures (*in situ* modification), or in already premodified form (see, for example, DE 40 04 781), i.e., the two reactants are reacted outside the actual compounding process.

[0023]   In addition to compounds exclusively containing the silicas according to the invention with and without organosilanes according to formulae I to III, the rubber compounds may additionally be reinforced with one or more fillers having a greater or lesser reinforcing action. It would primarily be customary in this connection to use a blend of carbon blacks (for example furnace, gas, flame, acetylene blacks) and the silicas according to the invention, with or without silane, but also of natural fillers, such as for example clays, siliceous chalks, other commercial silicas and the silicas according to the invention.

[0024] The blending ratio, as with the quantity of organosilane added, depends in this connection on the range of properties to be achieved in the finished rubber compound. A ratio of 5% to 95% between the silicas according to the invention and the other above-stated fillers, i.e., the silica according to the invention is 5% to 95% by weight of the mixture of fillers, is conceivable and is also achieved in this context.

[0025] Apart from the silicas according to the invention, the organosilanes and other fillers, the elastomers comprise a further important constituent of the rubber blend. The silicas according to the invention may be used in any types of rubber which may be vulcanized with accelerators/sulphur or also peroxide curable rubbers. Rubbers which may be cited in this connection are natural or synthetic elastomers, oil-extended or not, as a single polymer or blend with other rubbers such as for example natural rubbers, butadiene rubbers, isoprene rubbers, butadiene/styrene rubbers, in particular SBR produced using the solution polymerization process, butadiene/acrylonitrile rubbers, butyl rubbers, terpolymers of ethylene, propylene and unconjugated dienes.

[0026] The following additional rubbers may moreover also be considered for use in rubber compounds with the stated rubbers: carboxyl rubbers, epoxy rubbers, transpolypentenamers, halogenated butyl rubbers, 2-chlorobutadiene rubbers, ethylene/vinyl acetate copolymers, ethylene/propylene copolymers, optionally together with chemical derivatives of natural rubber and modified natural rubbers.

[0027] Customary further constituents such as plasticizers, stabilizers, activators, pigments, antioxidants and processing auxiliaries in customary quantities are also known.

[0028] The silicas according to the invention, with and without silane, may be used in any rubber applications, such as for example tires, conveyor belts, seals, V-belts, tubes, shoe soles etc.

[0029] Dispersion, i.e. the distribution of a substance (filler) in a polymer compound, is of vital significance to the subsequent properties of the article containing this substance. Tear strength values in particular (tensile strength, elongation at break, tear propagation resistance), but also hysteresis and abrasion values are highly dependent upon dispersion (Schweitzer *et al.*, *Rubber World* **138(6)**, 869 – 876, 1958; Schweitzer *et al.*, *Rubber World* **139(1)**, 74 – 81,1958; Hess *et al.*, *Rubber Chem. Tech.* **36(5)**, 1175 – 1229, 1963).

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[0030]   The significance of this parameter to rubber properties is accompanied by a lack of options for exactly measuring it, or many of the most commonly used methods allow only a subjective examination and assessment of dispersion.

[0031]   The most widely used methods for measuring dispersion are described in ASTM D 2663-88 and were all developed to measure the dispersion of carbon black in rubber, but may however also be used to measure the dispersion of silica-filled compounds, provided that the compound contains only this filler and not blends, for example carbon black and silica.

[0032]   One of the three methods described in the above-mentioned standard involves visual examination with the naked eye or slight magnification under the microscope and photographic recording of the vulcanizate samples, wherein the result is assessed against 5 standard photographs using a numbered scale from 1 to 5.

[0033]   Another method is to count filler agglomerates with a size of ≤5 μm. To this end, a microtome section of the vulcanizate is prepared and the percentage of the area occupied by these agglomerates is determined by transmission light microscopy. Here too, dispersion is divided into classes.

[0034]   The third option described is scanning the surface roughness of the vulcanizate with a needle. In this manner, the number and average height of surface roughness is measured. As with method 2, the roughness factor is converted into a dispersion index from very good to very poor.

[0035]   The microscopic method (for example 30 times magnification), in which dispersion in the vulcanizate is assessed against a numbered scale from 1 to 10 using 10 standard photographs is presently the most commonly used method, which, although subjective, is rapid, meaningful and most suited to laboratory operation.

[0036]   Dispersion and its evaluation described above constitute a property of the silica in the polymer compound. In order to be able to predict the subsequent dispersion behavior of a silica in the polymer compound before it is compounded, for example with rubber, the person skilled in the art makes use of the grindability of the silica. In other words, the grindability of the silica and its subsequent dispersion, for example in rubber, largely correlate.

[0037]   This grindability may *inter alia* be characterized by the energy required to achieve a particular particle fineness, or conversely by the particle fineness achieved when a

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grinder is operated at the same power and product throughput. The mill used is an Alpine-Kolloplex pin impact mill (Z 160) operated at a constant product throughput of 6 kg/h.

[0038]   Particle fineness is characterized by the average, volume-weighted particle diameter MTG (D(4.3)) measured by laser diffraction (Malvern Instruments, model 2600c).

[0039]   Values of ≤ 11 µm, in particular of ≤ 10 µm, are achieved for the silicas according to the invention, which are higher in customary silicas (≥ 12 µm). It has also been found that, due to the process by which the silicas are produced, the silicas according to the invention are already so fine that, in contrast with conventional products, they require no further grinding for many industrial applications and thus also offer economic advantages.

[0040]   The present invention also provides vulcanizable rubber compounds which contain the precipitated silicas according to the invention in quantities of 5 parts to 200 parts, related to 100 parts of rubber. Incorporation of this silica and production of the compounds containing this silica proceed in the manner customary in the rubber industry in an internal mixer or roll mill. The silica may be presented or used as powder, microbeads or granules. In this respect too, the silicas according to the invention do not differ from known, light silicate fillers.

[0041]   Due to the above-stated differences, the precipitated silicas according to the invention lead to improved dispersion properties at a constant surface area compared with standard silicas.

[0042]   The silicas according to the invention also exhibit better properties in relation to some other technically important rubber parameters. The following properties may be mentioned, higher modulus, lower tan δ as a measure of tire rolling resistance, better abrasion resistance, lower T-center values, better wet skid resistance, better rebound resilience, better heat build-up performance and better viscosity.

BRIEF DESCRIPTION OF THE FIGURES

[0043]   The drawings compare the essential physicochemical parameters of the precipitated silica according to the invention with those of known precipitated silica. The drawings show:

[0044]   Figure 1   the ratio of CTB to DBP

[0045]   Figure 2   the ratio of CTAB to DBP

[0046]   Figure 3   the ratio of CTAB to DBP

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[0047]	Figure 4	the ratio of CTAB to DBP
[0048]	Figure 5	the ratio of CTAB to V_2/V_1
[0049]	Figure 6	the ratio of CTAB to DBP/CTAB.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0050]   The following examples illustrate the invention:

The following substances are used in the examples:

First Latex Crepe	natural rubber
Ultrasil VN 2	precipitated silica (Degussa AG) with an N_2 surface area of 125 m^2/g
Ultrasil VN 3	precipitated silica (Degussa AG) with an N_2 surface area of 175 m^2/g
CBS	benzothiazyl-2-cyclohexylsulphenamide
TMTM	tetramethylthiuram monosulphide
Si 69	bis(3-triethoxysilylpropyl)tetrasilane (Degussa AG)
DEG	diethylene glycol
VSL 1955 S 25	solution polymerized styrene/ butadiene rubber with a styrene content of 25% and a vinyl content of 55% (Bayer AG)
DPG	diphenylguanidine
Vulkanox 4020	*N*-(1,3-dimethylbutyl)-*N*-phenyl-p-phenylenediamine (Bayer AG)
Protector G 35	ozone protective wax
ZBED	zinc dibenzylthiocarbamate
Buna CB 24	butadiene rubber from Bunawerke Hüls
Naftolene ZD	aromatic mineral oil plasticizer
Hisil 210	silica from PPG with an N_2 surface area of approx. 130 m^2/g
Hisil 255	silica from PPG with an N_2 surface area of approx. 170 m^2/g
KS 300	silica from Akzo with an N_2 surface area of approx. 125 m^2/g
KS 404	silica from Akzo with an N_2 surface area of approx. 175 m^2/g

[0051]   The following test standards were used:

Test	Unit	Standard
Tensile stress	MPa	DIN 53 504
Compression set B	%	ASTM D 395
Loss angle tan δ	–	DIN 53 513
DIN abrasion	mm^3	DIN 53 516
Firestone ball rebound	%	AD 20 405
Mooney viscosity	ME	DIN 53 523/524
Goodrich flexometer	°C	ASTM D 623 A

[0052]   EXAMPLE 1: Production of a silica according to the invention with an N_2 surface area in the range 100 m^2/g.

[0053]   43.5 m^3 of hot water is introduced into a vat and customary commercial sodium waterglass (weight modulus 3.42, density 1.348) is stirred in a quantity such that a pH of 8.5 is achieved. While maintaining a precipitation temperature of 88°C and pH 8.5, 16.8 m^3 of the same water glass and sulfuric acid (96%) are simultaneously added within 150 minutes from opposite positions. A solids content of 100 g/l is produced. Further sulfuric acid is then added until a pH of <5 is achieved. The solids are separated in presses, washed and the pressed paste dried by spray drying or in a rotary kiln and optionally ground.

[0054]   The precipitated silica obtained has an N_2 surface area of 80 m^2/g, an aggregate size of 1320 nm and grindability of 10 μm. The Sears value (V_2) is 4.4 ml/(1.5 g) and Hg porosimetry 2.7 ml/g. The CTAB surface area is 75 m^2/g. The DBP value is 236 ml/100 g. The V_2/V_1 ratio is 0.32. The DBP/CTAB ratio is 3.15.

[0055]   EXAMPLE 2: Production of a silica according to the invention with an N_2 surface area of the 100 m^2/g to 150 m^2/g range.

[0056]   The same procedure is used as in Example 1, with the exception that a pH value of 9.0 is maintained in the initial precipitation batch and during precipitation. After 135 minutes, a solids content of 98 g/l is achieved in the precipitation suspension.

[0057]   The precipitated silica obtained has an N_2 surface area of 120 m^2/g, grindability of 8.8 μm, a Sears value of 4.45 ml/(1.5 g) at an aggregate size of 490 nm and an

Hg pore volume of 2.85 ml/g. The DBP value is 270 ml/100 g. The CTAB surface area is 115 m^2/g. The V_2/V_1 ratio is 0.28. The DBP/CTAB ratio is 2.34.

[0058]   EXAMPLE 3: Production of a silica according to the invention with an N_2 surface area in the 150 m^2/g to 200 m^2/g range.

[0059]   The same procedure is used as in Example 2, with the difference that the precipitation time is shortened to 76 minutes and the precipitation temperature reduced to 80°C. After this period, a solids content in the precipitation suspension of 100 g/l is achieved. The precipitated silica obtained has the following physicochemical parameters: BET surface area of 184 m^2/g, grindability of 8.7 μm, Sears value of 7.5 ml/(1.5 g) at an aggregate size of 381 nm, Hg pore volume 2.26 ml/g. The CTAB surface area is 165 m^2/g. The DBP value is 255 ml/100 g. The V_2/V_1 ratio is 0.2080 to 0.2299. The DBP/CTAB ratio is 1.545.

[0060]   EXAMPLE 4: Determination of pore volume by Hg porosimetry on silicas according to the invention compared with some presently known commercial standard silicas

Process: Hg-Porosimetry according to DIN 66 133 but using an injection
                       process of from 7 bar to 500 bar

N_2 surface area (m^2/g): 100 to 150

Product Name	N_2 surface area (m^2/g)	Pore Volume (ml/g)
Hisil 210	130	1.54
KS 300	125	1.98
Ultrasil VN 2	125	1.82
Silica according to the invention (Example 2)	120	2.85

N_2 surface area (m^2/g): 150 to 200

Product Name	N_2 surface area (m^2/g)	Pore Volume (ml/g)
Hisil 225	170	1.13
KS 404	175	1.66
Ultrasil VN 3	175	1.46

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Silica according to the invention (Example 3)	184	2.26

[0061]   The silicas according to the invention have a distinctly higher pore volume.

[0062]   EXAMPLE 5: Comparison of Sears value (V_2) as a measure of the OH group density of the silicas according to the invention with standard commercial silicas

N_2 surface area (m^2/g): 100 to 150

Product Name	N_2 surface area [m^2/g]	V_2 [ml] = NaOH consumption [ml/(1.5 g)]
Hisil 210	130	8
KS 300	125	7.7
Ultrasil VN 2	125	7.2
Silica according to the invention (Example 2)	120	4.4

N_2 surface area (m^2/g): 150 to 200

Product Name	N_2 surface area [m^2/g]	V_2 [ml] = NaOH consumption [ml/(1.5 g)]
Hisil 255	170	8.1
KS 404	175	8.1
Ultrasil VN 3	175	9.9
Silica according to the invention (Example 3)	184	7.5

[0063]   The lower V_2 = NaOH consumption, the lower is the −OH group density. The comparison shows that the silicas according to the invention may have a silanol group density of up to 40% lower than known precipitated silicas.

[0064]   EXAMPLE 6: Determination of average aggregate size by photon correlation spectroscopy

Parameters:

Ultrasound time: 15 minutes

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Ultrasonic Device used: RK 510 H (manufacturer: Bandelin)

Suspending agent: Isopropanol/pentanol 10:1

Weight: 30 mg silica per 10 ml suspending agent

N_2 surface area (m^2/g): 100 to 150

Product Name	N_2 surface area (m^2/g)	Average aggregate size (nm)
Hisil 210	130	254
KS 300	125	197
Ultrasil VN 2	125	191
Silica according to the invention (Example 2)	120	490

N_2 surface area (m^2/g): 150 to 200

Product Name	N_2 surface area (m^2/g)	Average aggregate size (nm)
Hisil 255	170	152
KS 404	175	218
Ultrasil VN 3	175	167
Silica according to the invention (Example 3)	184	381

[0065]   The average aggregate size of the silicas according to the invention is distinctly greater than that of the known precipitated silicas.

EXAMPLE 7: Silica according to Example 2 of the invention in comparison with Ultrasil VN 2 in a natural rubber formulation with Si 69

	1	2
First Latex Crepe	100	100
Ultrasil VN 2	50	—
Silica according to the invention (Example 2)	—	50
ZnO RS	4	4

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Stearic acid	2	2
DEG	1	1
Si 69	3.2	3.2
CBS	1.6	1.6
TMTM	0.3	0.3
Sulfur	0.8	0.8
Mooney viscosity (MU)	77	69

Vulcanizate data: 150°C/$t_{95\%}$

	1	2
300% modulus (MPa)	8.1	9
Ball rebound (%)	56.8	58.6
DIN abrasion (mm³)	125	114
Goodrich flexometer (0.175", 108 N, RT, 18 h)		
T-center (°C)	81.2	70.8
tan δ/60°C	0.093	0.085

[0066]   In comparison with Ultrasil VN 2, which is comparable in surface area, the silica according to Example 2 of the invention leads to lower viscosities, higher modulus and resilience values, improved abrasion, lower heat build-up and lower loss angle tan at 60°C and thus lower rolling resistance.

[0067]   EXAMPLE 8: Silica according to the invention (Example 3) in comparison with Ultrasil VN 3 in a solution-SBR/BR tire tread formulation with Si 69

	1	2
VSL 1955 S 25	96	96
Buna CB 24	30	30
Ultrasil VN 3	80	–
Silica according to the invention (Example 3)	–	80

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ZnO RS	3	3
Stearic acid	2	2
Naftolen ZD	10	10
Vulkanox 4020	1.5	1.5
Protektor G 35	1	1
Si 69	6.4	6.4
CBS	1.5	1.5
DPG	2	2
ZBED	0.2	0.2
Sulfur	1.5	1.5
Mooney viscosity (MU)	72	68

Vulcanizate data: $150°C/t_{95\%}$

	1	2
300% modulus (MPa)	8.9	9.3
Ball rebound (%)	52.6	54.7
Loss tan δ according to DIN 53 513, device used: MTS		
tan δ/0°C	0.480	0.501
tan δ/60°C	0.152	0.144

[0068]   In comparison with VN 3, the silica according to the invention has lower viscosity, higher modulus, higher elasticity and, particularly importantly, higher wet skid resistance with low rolling resistance.

[0069]   EXAMPLE 9: Comparison of dispersion of silica according to the invention (Example 2) compared with VN 2 (identical N, surface area of approx. 120 m^2/g) (using the Philipps methods, described in technical information brochure 102 A).

[0070]   A piece of rubber approximately 20 to 30 μm in thickness (area approx. 5 x 5 mm^2) is cut using a Vibracut apparatus from FTB-Feinwerktechnik from a 6 mm sheet of vulcanizate of the formulation according to Example 8 filled with 80 parts of Ultrasil VN 2 or of the silica according to the invention from Example 2, related to 100 parts of rubber. This

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sample of rubber is transferred onto a glass slide and covered with a second glass slide. The sample prepared in this manner is examined under a light microscope with a reflected light attachment and reproduced as a negative image with 55-times magnification. A positive image with the desired final magnification is prepared from this negative.

[0071]   Dispersion is assessed according to the Philipps method using 10 standard photographs as stated below:

Number	Dispersion
1 to 2	very poor
3 to 4	poor
5 to 6	adequate
7 to 8	good
9 to 10	very good

[0072]   The dispersion of Ultrasil VN 2 is rated at 5 and is thus adequate, the dispersion of the silica according to the invention from Example 2 is rated at 9 and is thus very good.

[0073]   EXAMPLE 10: Comparison of dispersion of silica according to the invention from Example 3 with Ultrasil VN 3 (identical N_2 surface area of approx. 175 m^2/g). Formulation, procedure and assessment are performed in a similar manner to Example 9.

[0074]   The dispersion of Ultrasil VN 3 is rated at 2 and is thus very poor, the dispersion of the silica according to Example 3 of the invention is rated at 8 and is thus good.

[0075]   EXAMPLE 11: Determination of dispersion by roughness measurement using a Federal Dispersion Analysis EM D-4000-W7 unit. Comparison of Ultrasil VN 2 with the silica according to the invention from Example 2.

[0076]   A piece of rubber (20 mm x 2 mm) is cut using a cutting device also supplied by the above-stated equipment manufacturer from a 2 mm sheet of vulcanizate of the formulation according to Example 8 filled with 80 parts of Ultrasil VN 2 or with the silica according to the invention from Example 2, related to 100 parts of rubber, and is fixed into a holder provided by the equipment manufacturer. The surface of the vulcanizate is scanned using a diamond needle and the surface roughness caused by dispersion so determined. This

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process allows dispersion to be quantified as the device determines a value F^2H. F means the number of peaks and H their average height. Thus, the lower the value of this parameter, the better is the dispersion of the filler in the vulcanizate sample.

[0077]   For the above-stated fillers, the parameter F^2H gave the following values:

	Ultrasil VN 2	Silica according to the invention (Example 2)
F^2H	82366	32556

[0078]   The silica according to the invention thus has distinctly better dispersion. This method thus confirms the results from Example 9.

[0079]   EXAMPLE 12: Comparison of dispersion of Ultrasil VN 3 with the silica according to the invention from Example 3 using the roughness measurement from Example 11.

[0080]   The filling rate and procedure are here similar to those in Example 11.

	Ultrasil VN 3	Silica according to the invention (Example 3)
F^2H	55601	22602

[0081]   The silica according to the invention has distinctly better dispersion characteristics than VN 3. This method confirms the results found in Example 10.

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Attorney Docket No.: **021123-0238397**

ABSTRACT OF THE DISCLOSURE

A precipitated silica with the following physicochemical properties:

BET surface area	$35\ m^2/g$ to $350\ m^2/g$
BET/CTAB surface area ratio	0.8 to 1.1
Pore volume, PV	1.6 ml/g to 3.4 ml/g
Silanol group density ($V_2 = $ NaOH consumption)	$3\ ml/(1.5\ g)$ to $9.5\ ml/(1.5\ g)$
Average aggregate size	250 nm to 1500 nm
CTAB surface area	$30\ m^2/g$ to $350\ m^2/g$
DBP value	150 ml/100 g to 300 ml/100 g
V_2/V_1 by Hg porosimetry	0.19 to 0.46
DBP/CTAB	1.2 to 3.5

is produced by reacting alkali silicate with mineral acids at temperatures of 60°C to 95°C
while maintaining a pH of 7.5 to 10.5 and continuously stirring, continuing the reaction to a
solids concentration in the precipitation suspension of 90 g/l to 120 g/l, adjusting the pH
value to a value of less than or equal to 5, filtering out, washing, drying and optionally
grinding or granulating the precipitated silica. The precipitated silica is used as a filler in
vulcanizable rubber compounds and vulcanizates.

APPLICATION UNDER UNITED STATES PATENT LAWS

Attorney Docket No.   021123-0238397

Invention: PRECIPITATED SILICAS

Inventor(s):   ESCH *ET AL.*

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PILLSBURY WINTHROP LLP

This is a:

☐ Provisional Application

☐ Regular Utility Application

☐ Continuing Application

☐ PCT National Phase Application

☐ Design Application

☐ Reissue Application

☐ Plant Application

☐ Substitute Specification

☒ Marked up Specification

SPECIFICATION

30426921v1

PRECIPITATED SILICAS

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation of U.S. Patent Application Serial No. 08/594,327, filed January 30, 1996 (now abandoned), which is a continuation of U.S. Patent Application Serial No. 08/319,490, filed October 7, 1994 (now abandoned), which in turn claims priority to German Patent Application No. P 44 27 137.9, filed July 30, 1994 and German Patent Application No. P 43 34 201.9, filed October 7, 1993. All applications are incorporated herewith in their entirety by reference.

BACKGROUND OF THE INVENTION

1.   Field of the Invention:

[0001]   The present invention relates to precipitated silicas, to the process for the production thereof and to the use thereof in rubber compounds.

2.   Background of the Invention:

[0002]   Precipitated silicas may be incorporated into rubber compounds (S. Wolff, *Kautschuk und Gummikunstst. 7 (1988), p.674*) 41(7), 674 – 698. Known silicas may be only very poorly dispersed in rubber compounds, particularly at high filling rates. This poor dispersibility is one of the reasons why elevated silica filling rates are used only rarely in tire compounds. One reason for poor dispersibility may lie in the process by which the precipitated silicas are produced. Drying, poor grinding or also excessively hard granulation may lead to silica particles which cannot readily be dispersed (filler flecks). These flecks may be seen with the naked eye.

[0003]   Furthermore, silicas are highly polar and therefore have only poor phase compatibility with the non-polar polymers in the rubber compound. This form of dispersion occurs on the basis of the silica aggregates. It may only be evaluated using a light microscope and is known as microdispersion.

[0004]   Precipitated silicas which may be used as a filler in rubber compounds for tires are known from EP-A 0 520 862.

[0005]   A precipitated silica is known from published European Patent Application EP-A 0 157 703 which, according to EP-A 0 501 227, may be used as a filler in rubber compounds for tires.

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[0006]   Known precipitated silicas have the disadvantage that they exhibit poor microdispersion.

SUMMARY OF THE INVENTION

[0007]   The object of the invention is to provide a precipitated silica with optimum phase compatibility with rubber, polymer, and good microdispersion.

[0008]   The present invention provides a precipitated silica characterized by the following physicochemical properties:

BET surface area	35 m^2/g to 350 m^2/g
BET/CTAB surface area ratio	0.8 to 1.1
Pore volume, PV	1.6 ml/g to 3.4 ml/g
Silanol group density (V_2 = NaOH consumption)	~~6 to 20 ml~~ <u>3 ml/(1.5 g) to 9.5 ml/(1.5 g)</u>
Average aggregate size	250 nm to 1500 nm
CTAB surface area	30 m^2/g to 350 m^2/g
DBP value	150 $ml/100$ g to 300 ml/100 g
V_2/V_1 by Hg porosimetry	0.19 to 0.46 [,]
preferably	0.20 to 0.23
DBP/CTAB	1.2 to 3.5

[0009]   The physicochemical properties are determined using the following measurement methods:

BET surface area	Areameter, Ströhlein, to ISO 5794/ Annex D
Pore volume	Mercury porosimetry to DIN 66 133 <u>(7 bar to 2000 bar)</u>
Silanol group density	in Sears values, according to ~~G.W. Sears, Analyt. Chemistry 12, 1982-83 (1956)~~ <u>Sears. *Anal. Chem.* 28(12), 1981 – 1983, 1956.</u>
Average aggregate size	Photon correlation spectroscopy<u>, determined by Zeta Sizer 3 (manufacturer: Malvern Instruments)</u>
CTAB surface area	at pH 9, according to ~~Jay, Janzen and Kraus in Rubber Chemistry and Technology 44 (1971), 1287~~ <u>Janzen *et al.*, *Rubber Chem. Technol.* 44, 1287 – 1296, 1971.</u>
DBP value	ASTM D 2414-88

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Hg porosimetry   DIN 66 133

[0010]   The precipitated silica according to the invention may in particular have the following physicochemical parameters:

BET surface area [m²/g] (m²/g)	Hg porosimetry [ml/g] (ml/g)	Sears value V₂ NaOH (ml) [ml/(1.5 g)]	Average aggregate size [nm] (nm)
35 to [-] 100	2.5 to [-] 3.4	3 to 5.8 6-12	900 to [-] 1500
100 to [-] 150	2.4 to [-] 3.2	4 to 7.2 8-15	400 to [-] 850
150 to [-] 200	1.6 to [-] 2.4	5.3 to 9.1 11-19	300 to [-] 550
200 to [-] 350	1.6 to [-] 2.3	5.8 to 9.5 13-20	250 to [-] 520

[0011]   In a preferred embodiment, the precipitated silica according to the invention has good grindability. This characteristic is represented by the average particle size determined using Malvern laser diffraction (D(4.3)) of ≤11 µm, in particular of ≤10 µm, measured after grinding on an Alpine Kolloplex pin impact mill (Z 160) at a throughput of 6 kg/h.

[0012]   The present invention also provides a process for the production of the precipitated silica with the following physicochemical parameters

BET surface area	35 m²/g to 350 m²/g
BET/CTAB surface area ratio	0.8 to 1.1
Pore volume, PV	1.6 ml/g to 3.4 ml/g
Silanol group density (V₂ = NaOH consumption)	6 to 20 ml 3 ml/(1.5 g) to 9.5 ml/(1.5 g)
Average aggregate size	250 nm to 1500 nm
CTAB surface area	30 m²/g to 350 m²/g
DBP value	150 ml/100 g to 300 ml/100 g
V₂/V₁ by Hg porosimetry	0.19 to 0.46 [,]
preferably	0.20 to 0.23
DBP/CTAB	1.2 to 3.5

[0013]   which is characterized in that alkali silicate is reacted with mineral acids at temperatures of 60°C to 95°C while maintaining a pH of 7.5 to 10.5 and continuously

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stirring, the reaction is continued to a solids concentration in the precipitation suspension of 90 $\underline{g/l}$ to 120 g/1, the pH value is adjusted to a value of less than or equal to 5, the precipitated silica filtered out, washed, dried and optionally ground or granulated.

[0014]   In a preferred embodiment, customary commercial sodium water glass may be diluted with water to a pH of 8 to 9 and concentrated sulfuric acid and the same water glass solution may simultaneously be added to this diluted water glass solution which has an SiO_2 content of 4.9 g/1, while maintaining the pH value of 8 to 9.

[0015]   <u>Other preferred ranges of the pore volume ratio (V_2/V_1) are 0.19 to 0.43, 0.19 to 0.32, and 0.19 to 0.28.</u>

[0016]   Simultaneous addition of water glass solution and sulfuric acid may be performed over a period (duration of precipitation) of up to 160 minutes, preferably of greater than 90 minutes, in particular within 30 <u>minutes</u> to 90 minutes.

[0017]   Depending upon the duration of precipitation, differing BET surface areas of the precipitated silica may be achieved. Thus, at a duration of precipitation of more than 90 minutes, surface areas of 35 $\underline{m^2/g}$ to 150 m^2/g are achieved and, at a duration of 30 minutes to 90 minutes, surface areas of 150 $\underline{m^2/g}$ to 350 m^2/g.

[0018]   The precipitated silica according to the invention may be modified with organosilanes of the formulas I to III

$$[R^1{}_n\text{--}(RO)_{3\text{-}n}Si\text{--}(Alk)_m\text{--}(Ar)_p]_q[B] \qquad (I)$$

$$R^1{}_n\text{--}(RO)_{3\text{-}n}Si\text{--}(Alkyl) \qquad (II)$$

or

$$R^1{}_n\text{--}(RO)_{3\text{-}n}Si\text{--}(Alkenyl) \qquad (III)$$

in which:

B:	means $-SCN$, $-SH$, $-Cl$, $-NH_2$ (if q = 1) or $-S_x-$ (if q = 2) [,]
R and R^1:	mean an alkyl group with 1 to 4 carbon atoms, the phenyl residue, wherein all residues R and R^1 may each have the same or different meaning [,]
R:	means a C_1-C_4 alkyl, $\cancel{C_1\text{-}C_4}$ $\underline{C_1\text{-}C_4}$ alkoxy group [,]
n:	means 0, 1 or 2 [,]
Alk:	means a divalent unbranched or branched hydrocarbon residue with 1 to 6 carbon atoms [,]
m:	means 0 or 1 [,]

Ar:	means an arylene residue with 6 to 12 carbon atoms, preferably 6 carbon atoms [,]
p:	means 0 or 1, providing that p and n do not simultaneously mean 0 [,]
x:	means a number from 2 to 8 [,]
Alkyl:	means a monovalent unbranched or branched unsaturated hydrocarbon residue with 1 to 20 carbon atoms, preferably 2 to 8 carbon atoms [,]
Alkenyl:	means a monovalent unbranched or branched unsaturated hydrocarbon residue with 2 to 20 carbon atoms, preferably 2 to 8 carbon atoms [,]

[0019]   Modification with organosilanes may be performed in mixtures of 0.5 parts to 50 parts of organosilanes, related to 100 parts of precipitated silica, in particular of 2 parts to 15 parts, related to 100 parts of precipitated silica, wherein the reaction between the precipitated silica and silane may be performed during compounding (*in situ*) or outside the compounding process (premodified).

[0020]   In a preferred embodiment of the invention, bis(triethoxy-silylpropyl) tetrasulphane may be used as the silane.

[0021]   The precipitated silica according to the invention may be incorporated into vulcanizable rubber compounds as a reinforcing filler in quantities of 5 parts to 200 parts, related to 100 parts of rubber, as a powder, microbeads or granules both with and without silane modification.

[0022]   One or more of the above-stated silanes may be added, together with the silica according to the invention, to the rubber compound, wherein the reaction between the filler and silane proceeds during the compounding process at elevated temperatures (*in situ* modification), or in already premodified form (see, for example, ~~German patent~~ DE 40 04 781), i.e., the two reactants are reacted outside the actual compounding process.

[0023]   In addition to compounds exclusively containing the silicas according to the invention with and without organosilanes according to formulae I to III, the rubber compounds may additionally be reinforced with one or more fillers having a greater or lesser reinforcing action. It would primarily be customary in this connection to use a blend of carbon blacks (for example furnace, gas, flame, acetylene blacks) and the silicas according to the invention, with or without silane, but also of natural fillers, such as for example clays, siliceous chalks, other commercial silicas and the silicas according to the invention.

[0024]   The blending ratio, as with the quantity of organosilane added, depends in this connection on the range of properties to be achieved in the finished rubber compound. A ratio of 5—95% 5% to 95% between the silicas according to the invention and the other above-stated fillers, i.e., the silica according to the invention is 5—95% 5% to 95% by weight of the mixture of fillers, is conceivable and is also achieved in this context.

[0025]   Apart from the silicas according to the invention, the organosilanes and other fillers, the elastomers comprise a further important constituent of the rubber blend. The silicas according to the invention may be used in any types of rubber which may be vulcanized with accelerators/sulphur or also peroxide curable rubbers. Rubbers which may be cited in this connection are natural or synthetic elastomers, oil-extended or not, as a single polymer or blend with other rubbers such as for example natural rubbers, butadiene rubbers, isoprene rubbers, butadiene/styrene rubbers, in particular SBR produced using the solution polymerization process, butadiene/acrylonitrile rubbers, butyl rubbers, terpolymers of ethylene, propylene and unconjugated dienes.

[0026]   The following additional rubbers may moreover also be considered for use in rubber compounds with the stated rubbers: carboxyl rubbers, epoxy rubbers, transpolypentenamers, halogenated butyl rubbers, 2-chlorobutadiene rubbers, ethylene/vinyl acetate copolymers, ethylene/propylene copolymers, optionally together with chemical derivatives of natural rubber and modified natural rubbers.

[0027]   Customary further constituents such as plasticizers, stabilizers, activators, pigments, antioxidants and processing auxiliaries in customary quantities are also known.

[0028]   The silicas according to the invention, with and without silane, may be used in any rubber applications, such as for example tires, conveyor belts, seals, V-belts, tubes, shoe soles etc. [.]

[0029]   Dispersion, i.e. the distribution of a substance (filler) in a polymer compound, is of vital significance to the subsequent properties of the article containing this substance. Tear strength values in particular (tensile strength, elongation at break, tear propagation resistance), but also hysteresis and abrasion values are highly dependent upon dispersion (C.W. Schweitzer, W.M. Hess, J.E. Callun, Rubber World, 138, No. 6, 809 (1958) and 139, No. 1, 74 (1958)), (W.M. Hess, F.P. Ford, Rubber Chem. Tech., 36, No. 5, 1191 (1963)). (Schweitzer *et al., Rubber World* 138(6), 869 – 876, 1958; Schweitzer *et al., Rubber World* 139(1), 74 – 81, 1958; Hess *et al., Rubber Chem. Tech.* 36(5), 1175 – 1229, 1963).

[0030]   The significance of this parameter to rubber properties is accompanied by a lack of options for exactly measuring it, or many of the most commonly used methods allow only a subjective examination and assessment of dispersion.

[0031]   The most widely used methods for measuring dispersion are described in ASTM D 2663-88 and were all developed to measure the dispersion of carbon black in rubber, but may however also be used to measure the dispersion of silica-filled compounds, provided that the compound contains only this filler and not blends, for example carbon black and silica.

[0032]   One of the three methods described in the above-mentioned standard involves visual examination with the naked eye or slight magnification under the microscope and photographic recording of the vulcanizate samples, wherein the result is assessed against 5 standard photographs using a numbered scale from 1 to 5.

[0033]   Another method is to count filler agglomerates with a size of ≤ 5 μm. To this end, a microtome section of the vulcanizate is prepared and the percentage of the area occupied by these agglomerates is determined by transmission light microscopy. Here too, dispersion is divided into classes.

[0034]   The third option described is scanning the surface roughness of the vulcanizate with a needle. In this manner, the number and average height of surface roughness is measured. As with method 2, the roughness factor is converted into a dispersion index from very good to very poor.

[0035]   The microscopic method (for example 30 times magnification), in which dispersion in the vulcanizate is assessed against a numbered scale from 1 to 10 using 10 standard photographs is presently the most commonly used method, which, although subjective, is rapid, meaningful and most suited to laboratory operation.

[0036]   Dispersion and its evaluation described above constitute a property of the silica in the polymer compound. In order to be able to predict the subsequent dispersion behavior of a silica in the polymer compound before it is compounded, for example with rubber, the person skilled in the art makes use of the grindability of the silica. In other words, the grindability of the silica and its subsequent dispersion, for example in rubber, largely correlate.

[0037]   This grindability may *inter alia* be characterized by the energy required to achieve a particular particle fineness, or conversely by the particle fineness achieved when a

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grinder is operated at the same power and product throughput. The mill used is an Alpine-Kolloplex pin impact mill (Z 160) operated at a constant product throughput of 6 kg/h.

[0038]   Particle fineness is characterized by the average, volume-weighted particle diameter MTG (D(4.3)) measured by laser diffraction (Malvern Instruments, model 2600c).

[0039]   Values of ≤ 11 µm, in particular of ≤ 10 µm, are achieved for the silicas according to the invention, which are higher in customary silicas (≥ 12 µm). It has also been found that, due to the process by which the silicas are produced, the silicas according to the invention are already so fine that, in contrast with conventional products, they require no further grinding for many industrial applications and thus also offer economic advantages.

[0040]   The present invention also provides vulcanizable rubber compounds which contain the precipitated silicas according to the invention in quantities of 5 parts to 200 parts, related to 100 parts of rubber. Incorporation of this silica and production of the compounds containing this silica proceed in the manner customary in the rubber industry in an internal mixer or roll mill. The silica may be presented or used as powder, microbeads or granules. In this respect too, the silicas according to the invention do not differ from known, light silicate fillers.

[0041]   Due to the above-stated differences, the precipitated silicas according to the invention lead to improved dispersion properties at a constant surface area compared with standard silicas.

[0042]   The silicas according to the invention also exhibit better properties in relation to some other technically important rubber parameters. The following properties may be mentioned, higher modulus, lower tan δ as a measure of tire rolling resistance, better abrasion resistance, lower T-center values, better wet skid resistance, better rebound resilience, better heat build-up performance and better viscosity.

BRIEF DESCRIPTION OF THE FIGURES

[0043]   The drawings compare the essential physicochemical parameters of the precipitated silica according to the invention with those of known precipitated silica. The drawings show:

[0044]	Figure 1	the ratio of CTB to DBP
[0045]	Figure 2	the ratio of CTAB to DBP
[0046]	Figure 3	the ratio of CTAB to DBP

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[0047]   Figure 4   the ratio of CTAB to DBP

[0048]   Figure 5   the ratio of CTAB to V_2/V_1

[0049]   Figure 6   the ratio of CTAB to DBP/CTAB.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0050]   The following examples illustrate the invention:

The following substances are used in the examples:

First Latex Crepe	[-] natural rubber
Ultrasil VN 2	[-] precipitated silica (Degussa AG) with an N_2 surface area of 125 m^2/g
Ultrasil VN 3	[-] precipitated silica (Degussa AG) with an N_2 surface area of 175 m^2/g
CBS	[-] benzothiazyl-2-cyclohexylsulphenamide
TMTM	[-] tetramethylthiuram monosulphide
Si 69	[-] bis(3-triethoxysilylpropyl)tetrasilane (Degussa AG)
DEG	[-] diethylene glycol
VSL 1955 S 25	[-] solution polymerized styrene/ butadiene rubber with a styrene content of 25% and a vinyl content of 55% (Bayer AG)
DPG	[-] diphenylguanidine
Vulkanox 4020	[-] N-(1,3-dimethylbutyl)-N-phenyl-p-phenylenediamine (Bayer AG)
Protector G 35	[-] ozone protective wax
ZBED	[-] zinc dibenzylthiocarbamate
Buna CB 24	[-] butadiene rubber from Bunawerke Hüls
Naftolene ZD	[-] aromatic mineral oil plasticizer
Hisil 210	[-] silica from PPG with an N_2 surface area of approx. 130 m^2/g
Hisil 255	[-] silica from PPG with an N_2 surface area of approx. 170 m^2/g
KS 300	[-] silica from Akzo with an N_2 surface area of approx. 125 m^2/g

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KS 404   [-] silica from Akzo with an N_2 surface area of approx. 175 m^2/g

[0051]   The following test standards were used:

Test	Unit	Standard
Tensile stress	MPa	DIN 53 504
Compression set B	%	ASTM D 395
Loss angle tan δ	—	DIN 53 513
DIN abrasion	mm^3	DIN 53 516
Firestone ball rebound	%	AD 20 405
Mooney viscosity	ME	DIN 53 523/524
Goodrich flexometer	°C	ASTM D 623 A

[0052]   EXAMPLE 1: Production of a silica according to the invention with an N_2 surface area in the range 100 m^2/g.

[0053]   43.5 m^3 of hot water is introduced into a vat and customary commercial sodium waterglass (weight modulus 3.42, density 1.348) is stirred in a quantity such that a pH of 8.5 is achieved. While maintaining a precipitation temperature of 88°C and pH 8.5, 16.8 ~~16,8~~ m^3 of the same water glass and sulfuric acid (96%) are simultaneously added within 150 minutes from opposite positions. A solids content of 100 g/l is produced. Further sulfuric acid is then added until a pH of <5 is achieved. The solids are separated in presses, washed and the pressed paste dried by spray drying or in a rotary kiln and optionally ground.

[0054]   The precipitated silica obtained has an N_2 surface area of 80 m^2/g, an aggregate size of 1320 nm and grindability of 10 μm. The Sears value (V_2) is 4.4 ml/(1.5 g) ~~9.0 ml~~ and Hg porosimetry 2.7 ml/g. The CTAB surface area is 75 m^2/g. The DBP value is 236 ml/100 g. The V_2/V_1 ratio is 0.32 ~~The V_2/V_1 ratio is ...~~. The DBP/CTAB ratio is 3.15 ~~The DBP/CTAB ratio is ...~~.

[0055]   EXAMPLE 2: Production of a silica according to the invention with an N_2 surface area of the ~~100 - 150 m^2/g~~ 100 m^2/g to 150 m^2/g range.

[0056]   The same procedure is used as in Example 1, with the exception that a pH value of 9.0 is maintained in the initial precipitation batch and during precipitation. After 135 minutes, a solids content of 98 g/l is achieved in the precipitation suspension.

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[0057]   The precipitated silica obtained has an N_2 surface area of 120 m^2/g, grindability of 8.8 μm, a Sears value of <u>4.45 ml/(1.5 g)</u> ~~9.1 ml~~ at an aggregate size of 490 nm and an Hg pore volume of 2.85 ml/g. The DBP value is 270 ml/100 g. The CTAB surface area is 115 m^2/g. <u>The V_2/V_1 ratio is 0.28.</u> ~~The V_2/V_1 ratio is ...~~ The DBP/CTAB ratio is 2.34.

[0058]   EXAMPLE 3: Production of a silica according to the invention with an N_2 surface area in the ~~150—200 m^2/g~~ <u>150 m^2/g to 200 m^2/g</u> range.

[0059]   The same procedure is used as in Example 2, with the difference that the precipitation time is shortened to 76 minutes and the precipitation temperature reduced to 80°C. After this period, a solids content in the precipitation suspension of 100 g/l is achieved. The precipitated silica obtained has the following physicochemical parameters: BET surface area <u>of</u> 184 m^2/g, grindability of 8.7 μm, Sears value <u>of 7.5 ml/(1.5 g)</u> ~~15.7 ml~~ at an aggregate size of 381 nm, Hg pore volume 2.26 ml/g. The CTAB surface area is 165 m^2/g. The DBP value is 255 ml/100 g. The V_2/V_1 ratio is 0.2080 to 0.2299. The DBP/CTAB ratio is 1.545.

[0060]   EXAMPLE 4: Determination of pore volume by Hg porosimetry on silicas according to the invention compared with some presently known commercial standard silicas

Process: Hg-Porosimetry according to DIN 66 133 but using an injection process ~~7-500 bar~~ <u>of from 7 bar to 500 bar</u>

N_2 surface area (m^2/g): <u>100 to 150</u> ~~100-150~~

Product Name	N_2 surface area (m^2/g)	Pore Volume (ml/g)
Hisil 210	130	1.54
KS 300	125	1.98
Ultrasil VN 2	125	1.82
Silica according to the invention (Example 2)	120	2.85

N_2 surface area (m^2/g): <u>150 to 200</u> ~~150-200~~

Product Name	N_2 surface area (m^2/g)	Pore Volume (ml/g)
Hisil 225	170	1.13

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KS 404	175	1.66
Ultrasil VN 3	175	1.46
Silica according to the invention (Example 3)	184	2.26

[0061]   The silicas according to the invention have a distinctly higher pore volume.

[0062]   EXAMPLE 5: Comparison of Sears value (V_2) as a measure of the OH group density of the silicas according to the invention with standard commercial silicas

N_2 surface area (m²/g): <u>100 to 150</u> ~~100-150~~

Product Name	N_2 surface area [m²/g] ~~(m²/g)~~	V_2 [ml] ~~(ml)~~ = NaOH consumption [ml/(1.5 g)] ~~(ml/g)~~
Hisil 210	130	~~16.8~~ <u>8</u>
KS 300	125	~~16.1~~ <u>7.7</u>
Ultrasil VN 2	125	~~15~~ <u>7.2</u>
Silica according to the invention (Example 2)	120	~~9.1~~ <u>4.4</u>

N_2 surface area (m²/g): <u>150 to 200</u> ~~150-200~~

Product Name	N_2 surface area [m²/g] ~~(m²/g)~~	V_2 [ml] ~~(ml)~~ = NaOH consumption [ml/(1.5 g)] ~~(ml/g)~~
Hisil 255	170	~~16.9~~ <u>8.1</u>
KS 404	175	~~16.9~~ <u>8.1</u>
Ultrasil VN 3	175	~~20.7~~ <u>9.9</u>
Silica according to the invention (Example 3)	184	~~15.7~~ <u>7.5</u>

[0063]   The lower V_2 = NaOH consumption, the lower is the <u>OH</u> ~~OH~~ group density. The comparison shows that the silicas according to the invention may have a silanol group density of up to 40% lower than known precipitated silicas.

[0064]   EXAMPLE 6: Determination of average aggregate size by photon correlation spectroscopy

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Parameters:

Ultrasound time: 15 ['] minutes

Ultrasonic Device used: RK 510 H (manufacturer: Bandelin)

Suspending agent: Isopropanol/pentanol 10:1

Weight: 30 mg silica per 10 ml suspending agent

N_2 surface area (m^2/g): 100 to 150 ~~100 150~~

Product Name	N_2 surface area (m^2/g)	Average aggregate size (nm)
Hisil 210	130	254
KS 300	125	197
Ultrasil VN 2	125	191
Silica according to the invention (Example 2)	120	490

N_2 surface area (m^2/g): 150 to 200 ~~150 200~~

Product Name	N_2 surface area (m^2/g)	Average aggregate size (nm)
Hisil 255	170	152
KS 404	175	218
Ultrasil VN 3	175	167
Silica according to the invention (Example 3)	184	381

[0065]   The average aggregate size of the silicas according to the invention is distinctly greater than that of the known precipitated silicas.

[0066]   EXAMPLE 7: Silica according to Example 2 of the invention in comparison with Ultrasil VN 2 in a natural rubber formulation with Si 69

	1	2
First Latex Crepe	100	100
Ultrasil VN 2	50	—

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Silica according to ~~Example 2 of~~ the invention (Example 2)	–	50
ZnO RS	4	4
Stearic acid	2	2
DEG	1	1
Si 69	3.2	3.2
CBS	1.6	1.6
TMTM	0.3	0.3
Sulfur	0.8	0.8
Mooney viscosity (MU)	77	69

Vulcanizate data: 150°C/$t_{95\%}$

	<u>1</u>	<u>2</u>
300% modulus (MPa)	8.1	9
Ball rebound (%)	56.8	58.6
DIN abrasion (mm^3)	125	114
Goodrich flexometer (0.175", 108 N, RT, 18 h)		
T-center (°C)	81.2	70.8
~~MTS (DIN 53 513)~~		
<u>Loss tan δ according to DIN 53 513, device used: MTS</u>		
tan δ/60°C	<u>0.093</u>	<u>0.085</u>

[0067]   In comparison with Ultrasil VN 2, which is comparable in surface area, the silica according to Example 2 of the invention leads to lower viscosities, higher modulus and resilience values, improved abrasion, lower heat build-up and lower loss angle tan at 60°C and thus lower rolling resistance.

[0068]   EXAMPLE 8: Silica according to the invention (Example 3) in comparison with Ultrasil VN 3 in a solution-SBR/BR tire tread formulation with Si 69

	1	2

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VSL 1955 S 25	96	96
Buna CB 24	30	30
Ultrasil VN 3	80	—
Silica according to the invention (Example 3)	—	80
ZnO RS	3	3
Stearic acid	2	2
Naftolen ZD	10	10
Vulkanox 4020	1.5	1.5
Protektor G 35	1	1
Si 69	6.4	6.4
CBS	1.5	1.5
DPG	2	2
ZBED	0.2	0.2
Sulfur	1.5	1.5
Mooney viscosity (MU)	72	68

Vulcanizate data: $150°C/t_{95\%}$

	1	2
300% modulus (MPa)	8.9	9.3
Ball rebound (%)	52.6	54.7
~~MTS (DIN 53 513)~~		
Loss tan δ according to DIN 53 513, device used: MTS		
tan δ/0°C	0.480	0.501
tan δ/60°C	0.152	0.144

[0069]   In comparison with VN 3, the silica according to the invention has lower viscosity, higher modulus, higher elasticity and, particularly importantly, higher wet skid resistance with low rolling resistance.

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[0070]   EXAMPLE 9: Comparison of dispersion of silica according to the invention (Example 2) compared with VN 2 (identical N_2 surface area of approx. 120 m^2/g) (using the Philipps methods, described in technical information brochure 102 A).

[0071]   A piece of rubber approximately ~~20-30 µm~~ 20 to 30 µm in thickness (area approx. 5 x 5 $\underline{mm^2}$ ~~mm~~) is cut using a Vibracut apparatus from FTB-Feinwerktechnik from a 6 mm sheet of vulcanizate of the formulation according to Example 8 filled with 80 parts of Ultrasil VN 2 or of the silica according to the invention from Example 2, related to 100 parts of rubber. This sample of rubber is transferred onto a glass slide and covered with a second glass slide. The sample prepared in this manner is examined under a light microscope with a reflected light attachment and reproduced as a negative image with 55-times magnification. A positive image with the desired final magnification is prepared from this negative.

[0072]   Dispersion is assessed according to the Philipps method using 10 standard photographs as stated below:

Number	Dispersion
~~1-2~~ 1 to 2	very poor
~~3-4~~ 3 to 4	poor
~~5-6~~ 5 to 6	adequate
~~7-8~~ 7 to 8	good
~~9-10~~ 9 to 10	very good

[0073]   The dispersion of Ultrasil VN 2 is rated at 5 and is thus adequate, the dispersion of the silica according to the invention from Example 2 is rated at 9 and is thus very good.

[0074]   EXAMPLE 10: Comparison of dispersion of silica according to the invention from Example 3 with Ultrasil VN 3 (identical N_2 surface area of approx. 175 m^2/g). Formulation, procedure and assessment are performed in a similar manner to Example 9.

[0075]   The dispersion of Ultrasil VN 3 is rated at 2 and is thus very poor, the dispersion of the silica according to Example 3 of the invention is rated at 8 and is thus good.

[0076]   EXAMPLE 11: Determination of dispersion by roughness measurement using a Federal Dispersion Analysis EM D-4000-W7 unit. Comparison of Ultrasil VN 2 with the silica according to the invention from Example 2.

[0077]   A piece of rubber (20 mm x 2 mm) is cut using a cutting device also supplied by the above-stated equipment manufacturer from a 2 mm sheet of vulcanizate of the formulation according to Example 8 filled with 80 parts of Ultrasil VN 2 or with the silica according to the invention from Example 2, related to 100 parts of rubber, and is fixed into a holder provided by the equipment manufacturer. The surface of the vulcanizate is scanned using a diamond needle and the surface roughness caused by dispersion so determined. This process allows dispersion to be quantified as the device determines a value F^2H. F means the number of peaks and H their average height. Thus, the lower the value of this parameter, the better is the dispersion of the filler in the vulcanizate sample.

[0078]   For the above-stated fillers, the parameter F^2H gave the following values:

	Ultrasil VN 2	Silica according to the invention (Example 2)
F^2H	82366	32556

[0079]   The silica according to the invention thus has distinctly better dispersion. This method thus confirms the results from Example 9.

[0080]   EXAMPLE 12: Comparison of dispersion of Ultrasil VN 3 with the silica according to the invention from Example 3 using the roughness measurement from Example 11.

[0081]   The filling rate and procedure are here similar to those in Example 11.

	Ultrasil VN 3	Silica according to the invention (Example 3)
F^2H	55601	22602

[0082]   The silica according to the invention has distinctly better dispersion characteristics than VN 3. This method confirms the results found in Example 10.

~~BRIEF DESCRIPTION OF THE FIGURES OF DRAWING~~

~~The drawings compare the essential physicochemical parameters of the precipitated silica according to the invention with those of known precipitated silica. The drawings show:~~

~~Figure 1   the ratio of CTB to DBP~~

~~Figure 2 to 4   the ratio of CTAB to DBP~~

~~Figure 5   the ratio of CTAB to DBP to V2/V1~~

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~~Figure 6~~   ~~the ratio of CTAB to DBP/CTAB.~~

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ABSTRACT OF THE DISCLOSURE

A precipitated silica with the following physicochemical properties:

BET surface area	35 m^2/g to 350 m^2/g
BET/CTAB surface area ratio	0.8 to 1.1
Pore volume, PV	1.6 ml/g to 3.4 ml/g
Silanol group density (V_2 = NaOH consumption)	~~6 to 20 ml~~ 3 ml/(1.5 g) to 9.5 ml/(1.5 g)
Average aggregate size	250 nm to 1500 nm
CTAB surface area	30 m^2/g to 350 m^2/g
DBP value	150 ml/100 g to 300 ml/100 g
V_2/V_1 by Hg porosimetry	0.19 to 0.46
DBP/CTAB	1.2 to 3.5

is produced by reacting alkali silicate with mineral acids at temperatures of 60°C to 95°C while maintaining a pH of 7.5 to 10.5 and continuously stirring, continuing the reaction to a solids concentration in the precipitation suspension of 90 g/l to 120 g/l, adjusting the pH value to a value of less than or equal to 5, filtering out, washing, drying and optionally grinding or granulating the precipitated silica. The precipitated silica is used as a filler in vulcanizable rubber compounds and vulcanizates.